

154. *The Tautomerism of Arene and Ditertiary Phosphine Complexes of Ruthenium(0), and the Preparation of New Types of Hydrido-complexes of Ruthenium(II).**

By J. CHATT and J. M. DAVIDSON.

The reduction of *trans*-[RuCl₂(PP)₂] (PP = Me₂P·CH₂·CH₂·PMe₂) by "arene" negative ions (arene = benzene, naphthalene, anthracene, and phenanthrene) has given a new series of hydrido(aryl)-complexes typified by *cis*-[RuH(2-C₁₀H₇)(PP)₂] (Ia). Members have been characterised from their physical properties, particularly infrared and n.m.r. spectra, and their chemical reactions. Although (Ia) is a hydridic reducing agent and reduces bromoethane to ethane, it is in tautomeric equilibrium with a finite concentration of [Ru(C₁₀H₈)(PP)₂] (Ib) which probably contains ruthenium(0) and is so reactive that its reactions predominate in those of the complex.

Pyrolysis of (I) gives naphthalene and [Ru(PP)₂] (II) which has similarly dual properties. Its physical properties are consistent with the formulation [Ru^{II}H(CH₂·PMe·CH₂·CH₂·PMe₂)(PP)], and its chemistry with [Ru⁰(PP)₂]. This is a new class of compound in which hydride transfer has taken place from an alkyl side-chain of the ligand to the metal atom.

Products of the reactions of (I) and (II) with deuterium chloride have been analysed by mass spectrography, and it has been demonstrated unequivocally that hydrido-ruthenium(II) complexes and their ruthenium(0) tautomers are present in solutions of both complexes. Isotopic tracing methods show that the Ru-H bond in the naphthyl complex is formed by attack at the 2-position in naphthalene, and in [Ru(PP)₂] at a methyl group in the ditertiary phosphine ligand.

Other low-valent ruthenium complexes, *e.g.*, [Ru(PP)₂]²⁻, have been obtained as intermediates in the synthesis of *cis*-[RuH₂(PP)₂] (III).

THE lowest oxidation states of the transition metals are stabilised by complex-formation with a group of ligands which are feebly basic or non-basic, electrically neutral, and have

* Presented at the XIXth International Congress of I.U.P.A.C., London, 1963.

unfilled atomic or molecular orbitals of suitable symmetry and energy to combine with the filled *d*-orbitals of the metal atom.¹ Thus, ligands such as carbon monoxide, tertiary phosphines, and unsaturated and aromatic hydrocarbons can form multiple bonds of low polarity with metals in co-ordination compounds and can stabilise low-valent states. However, with carbon monoxide and unsaturated ligands, polymerisation and carbonylation often occur and complicated products usually result. The tertiary phosphines normally give mononuclear complexes of the zerovalent metals. Thus, octahedral complexes of the type $[M^0(PP)_3]$ ($M = V, Cr, Mo, W$; $PP = Me_2P \cdot CH_2 \cdot CH_2 \cdot PMe_2$), and tetrahedral complexes of the type $[M^0(PP)_2]$ ($M = Co, Ni, Pd, Pt$), have been prepared by the reduction of metal halides in the presence of the tertiary phosphine.²⁻⁴ Chatt and Watson⁴ observed that, although *trans*- $[FeCl_2(PP)_2]$ was reduced by sodium-naphthalene to the expected planar $[Fe^0(PP)_2]$, a hydride abstraction reaction took place when the ruthenium and osmium analogues were reduced; the products retained the naphthalene nucleus.⁴ This Paper presents details of these phenomena.

They are particularly interesting because in recent years it has become evident that hydrogen atoms in the skeleton of hydrocarbon ligands may become mobile in the presence of transition metals with filled *d*-orbitals. For example, both intermolecular and intramolecular hydrogen transfer is readily promoted in unsaturated alcohols by the presence of ruthenium trichloride, with the formation of olefins and aldehydes.⁵ The double bond of olefins readily migrates in the presence of many transition-metal halides,⁶ and with Na_2PdCl_4 in acetic acid it occurs through the stepwise migration of a hydrogen atom from one carbon atom to its nearest neighbour.⁷ A similar hydrogen migration occurs in the conversion of olefins into alkenyl acetates by palladium chloride in acetic acid,⁸ and in the conversion of ethylenepalladous chloride into acetaldehyde free from deuterium, by deuterium oxide.⁹ In this type of reaction the hydrogen undergoing migration does not exchange with the solvent, suggesting that the migration occurs through the metal. From the very low C-H stretching frequencies and high chemical shifts associated with certain hydrogen atoms in some hydrocarbon ligands attached to transition metals it seems that the hydrogen atoms and the metal interact, while still remaining attached to the carbon of the hydrocarbon ligand.¹⁰ Perhaps they interact in the manner proposed for the *N*-hydrogen atoms of co-ordinated amines with such metals as platinum(II).¹¹

We now report a readily reversible interaction in which the hydrogen atom from an aromatic hydrocarbon ligand passes completely to the metal but is sufficiently labile to return to the co-ordinated hydrocarbon residue, giving a novel tautomerism [eqn. (11), p. 849]. In the absence of the hydrocarbon a similar tautomerism exists, involving a hydrogen atom of a methyl group in a tertiary phosphine ligand [eqn. (12), p. 849].

The evidence for the tautomerism is as follows: when *cis*- or *trans*- $[RuCl_2(PP)_2]$ was reduced by arene negative ions in tetrahydrofuran solution, complexes $[Ru(arene)(PP)_2]$, whose physical properties are consistent with the general formulation *cis*- $[Ru^{II}H(aryl)(PP)_2]$ (*aryl* = phenyl, 2-naphthyl, anthryl, and phenanthryl), are formed. Nevertheless, most of their chemical reactions are consistent with the formulation $[Ru^0(arene)(PP)_2]$. These hydrido-organocomplexes are diamagnetic non-electrolytes soluble in hydrocarbon and ether solvents, and, except for the orange anthracene derivative, are colourless. The dry

¹ Chatt, *J. Inorg. Nuclear Chem.*, 1958, **8**, 515.

² Chatt and Rowe, *Nature*, 1961, **191**, 1191.

³ Chatt, Hart, and Watson, *J.*, 1962, 2537.

⁴ Chatt and Watson, *J.*, 1962, 2545.

⁵ Nicholson and Shaw, *Proc. Chem. Soc.*, 1963, 282.

⁶ British Petroleum Co. Ltd., Belg. Pat. 612,300/1962 (*Chem. Abs.*, 1962, **57**, 13,605a).

⁷ Davies, *Austral. J. Chem.*, 1964, **17**, 212.

⁸ Stern, *Proc. Chem. Soc.*, 1963, 111.

⁹ Smidt, Hafner, Jira, Sieber, Sedlmeier, and Sabel, *Angew. Chem. (Internat. Edn.)*, 1962, **1**, 80; Smidt, *Chem. and Ind.*, 1962, 54.

¹⁰ Winkhaus, Pratt, and Wilkinson, *J.*, 1961, 3807, and references therein.

¹¹ Chatt, Duncanson, and Venanzi, *J.*, 1955, 4461; *J. Inorg. Nuclear Chem.*, 1958, **8**, 67.

TABLE 1.

	Compound	M. p.	Infrared spectra.				$\delta(\text{C-H})$ (aromatic)
			μ (D)	$\nu(\text{Ru-H})$	$\nu(\text{Ru-D})$	$\nu(\text{C-C})$ (aromatic)	
(I)	<i>cis</i> -[RuH(2-C ₁₀ H ₇)(Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂]	182°	6.00	1802s	—	1605w, 1565m, 1546w	814vs, 737s
(II)	[Ru(Me ₂ P-CH ₂ -CH ₂ -PMe ₂) ₂]	269—271	1.5 *	1791s, 1815sh	—	—	—
(III)	<i>cis</i> -[RuH ₂ (Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂]	82	3.15	1806vs	(1303) ^d	—	—
(IV)	<i>cis</i> -[RuH(C ₆ H ₅)(Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂]	136—138	5.3 *	1806s	—	1560m, 1548w, sh	730vs, 692s, sh
(V)	<i>cis</i> -[RuH(C ₁₄ H ₉)(Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂]	185—187	6.35 *	1802s	—	1622w, 1601m, 1560w	740vs, 705s, 686s
(VI)	<i>cis</i> -[RuH(C ₁₄ H ₉)(Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂]	202	6.25 *	1796s	—	1602w, 1573m, 1553w	751s
		decomp. >185					
(VII)	<i>cis</i> -[RuH(C ₁₀ H ₈ D)(Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂] ^c	180—182	—	1802s	—	—	—
(VIII)	<i>cis</i> -[RuD(2-C ₁₀ H ₇)(Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂]	180—182	—	1803vw ^e	1294s	1586m, 1541w, 1521w	—
(IX)	<i>cis</i> -[RuD(2-C ₁₀ H ₇)(CD ₃) ₂ P-CD ₂ -CD ₂ -P(CD ₃) ₂] ₂]	181—184	—	1803vw ^e	1296s	1572m, 1529w, 1511w	—
(X)	[Ru(CD ₃) ₂ P-CD ₂ -CD ₂ -P(CD ₃) ₂]	265—268	—	1797vw ^e	1291s, 1311sh	—	—
(XI)	<i>cis</i> -[RuH(2-C ₁₀ H ₇)(CD ₃) ₂ P-CD ₂ -CD ₂ -P(CD ₃) ₂]	180—185	—	1789s	—	1603w, 1563m, 1543m	811vs, 734s
(XII)	[Ru(Me ₂ P-CD ₂ -CD ₂ -PMe ₂) ₂]	269—273	—	1794s, 1823sh	—	—	—
(XIII)	<i>cis</i> -[RuH(2-C ₁₀ H ₇)(Me ₃ P-CD ₂ -CD ₂ -PMe ₂) ₂]	185—187	—	1789s	—	1600m, 1560m, 1541m	810vs, 735s
(XIV)	<i>trans</i> -[RuBr(2-C ₁₀ H ₇)(Me ₃ P-CH ₂ -CH ₂ -PMe ₂) ₂] ^f	294 (decomp.)	2.3 *	—	—	1600w, 1563m, 1541w	813vs, 730vs

* Determined using estimated values of refractivity and density. ^a C₁₄H₉ = Anthryl. ^b C₁₄H₉ = Phenanthryl. ^c Mixed isomers from 2-deuterionaphthalene, including [RuD(C₁₀H₇)(PP)₂]. ^d In *cis*-[RuHD(Me₃P-CH₂-CH₂-PMe₂)₂]. ^e Residual hydrogen. ^f Also has 1 mol. of C₆H₆ of crystallisation with $\delta(\text{C-H})$ at 671 cm.⁻¹.

TABLE 3.

Reactions of complexes of ruthenium with hydrogen chloride and deuterium chloride.

Compound	Sample size (mg.)	Added HCl (ml. s.t.p.)	Added DCl (ml. s.t.p.)	Recovered HCl titre vs. N/20 KOH	H ₂ (or isotopes) evolved	Ratio Ru : H ₂	Ratio HCl : H ₂	Isotopic constitution (vol. %)		Atom fraction of H (x)
								D ₂	H ₂	
<i>cis</i> -[RuH(2-C ₁₀ H ₇)(PP) ₂] (I) ^a	38.9	9.23	—	5.39	1.60	0.97	2.02	77.1	—	—
"	250.7	—	24.3	—	10.6	1.00	—	74.0	0.8	0.13
"	20.8	—	1.93	—	0.881	1.00	—	73.7	1.2	0.14
"	70	—	39.8	—	—	—	—	—	2.0	0.14
<i>cis</i> -[RuH(C ₁₀ H ₈ D)(PP) ₂] (VII) ^b	27.1	2.94	—	—	1.11	0.97	—	0.2	92.4	0.961
<i>cis</i> -[RuH(C ₆ H ₅)(PP) ₂] (IV)	36.3	7.28	—	3.44	1.58	0.93	2.17	—	—	—
<i>cis</i> -[RuH(C ₁₄ H ₉)(PP) ₂] (V) ^c	98.2	11.1	—	3.63	3.45	0.91	2.03	—	—	—
[Ru(PP) ₂] (II) ^d	24.9	9.64	—	6.12	1.44	1.03	1.95	—	—	—
"	30.1	—	3.67	—	1.70	1.01	—	69.6	2.9	0.17
"	28.2	—	3.42	—	1.62	1.03	—	63.9	2.7	0.20
<i>trans</i> -[RuHCl(PP) ₂]	95.7	8.42	—	3.25	5.09	1.03	0.94	—	—	—
<i>trans</i> -[RuHBr(PP) ₂]	36.5	—	1.84	—	1.70	1.00	—	18.2	23.2	(0.45)
<i>cis</i> -[RuH ₂ (PP) ₂] (III)	39.4	8.76	—	3.94	4.36	2.00	0.99	—	—	—
"	12.9	—	1.43	—	1.45	2.02	—	27.4	49.0	23.6

^a From solid residue involatile at —5° was sublimed 55.4 mg. naphthalene (91.5%) containing 38 ± 2% of C₁₀H₇D. ^b Mixture of 4 isomers prepared from 2-C₁₀H₇D (84 ± 4% with mass no. 129). ^c C₁₄H₉ = Anthryl. ^d In a similar experiment 26.2 mg. of [Ru(PP)₂] gave an involatile solid residue of *cis*-[RuCl₂(PP)₂] (crude yield 32.5 mg., 105%). ^e Duplicate experiment carried out in homogenous liquid phase at 24° in presence of naphthalene (9.3 mg.) which was recovered unchanged.

solids are oxidised slowly in the air, but solutions are rapidly decomposed. Because our method of analysis was a series of degradations, the naphthalene compound $[\text{RuC}_{10}\text{H}_8(\text{PP})_2]$ (I) was chosen for detailed study since naphthalene can readily be isolated from small-scale reaction mixtures by simple fractional sublimation and fractional condensation procedures.

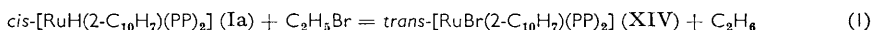
$[\text{RuC}_{10}\text{H}_8(\text{PP})_2]$ (I) has a complex infrared spectrum (Table 1) in which the strong band at 1802 cm^{-1} may be assigned to the Ru-H stretching mode of the form *cis*- $[\text{RuH}(2\text{-C}_{10}\text{H}_7)(\text{PP})_2]$ (Ia). Absorption from the naphthalene has undergone profound modification. The characteristic C-H deformation mode at 780 cm^{-1} is absent and is replaced by two at 737 and 814 cm^{-1} . Around $1550\text{--}1600\text{ cm}^{-1}$ appear a group of sharp bands from the C-C ring vibration indicative of the naphthyl group as distinct from the neutral hydrocarbon. The n.m.r. spectrum (Table 2), recorded in $[\text{H}_8]\text{tetrahydrofuran}$,

TABLE 2.
Nuclear magnetic resonance spectra.

	Compound	$\tau(\text{C-H})_{\text{ar}}$	$\tau(\text{C-H})_{\text{al}}$	$\tau\text{Ru-H}$	$I(\text{H}_{\text{al}})/I(\text{H}_{\text{ar}})$
(I)	<i>cis</i> - $[\text{RuH}(2\text{-C}_{10}\text{H}_7)(\text{PP})_2]$	2.37	8.69	17.6, 19.8	4.6 ± 0.2^b
(III)	<i>cis</i> - $[\text{RuH}_2(\text{PP})_2]$	—	—	18.6	—
(IV)	<i>cis</i> - $[\text{RuH}(\text{C}_6\text{H}_5)(\text{PP})_2]$	2.37, 3.44	8.65	—	6.6 ± 0.1^b
(V)	<i>cis</i> - $[\text{RuH}(\text{C}_{14}\text{H}_9)(\text{PP})_2]^a$	2.25	8.64	—	3.5 ± 0.1^b

^a $\text{C}_{14}\text{H}_9 = \text{Anthryl}$. ^b In $[\text{H}_8]\text{tetrahydrofuran}$.

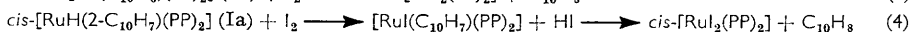
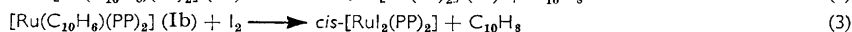
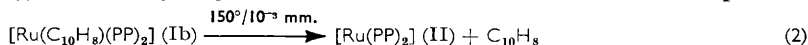
showed three complex multiplets at $\tau = 2.37$ ($\text{C}_{\text{ar}}\text{-H}$), 8.69 ($\text{C}_{\text{aliph}}\text{-H}$), and 18.6 (two doublets, Ru-H). The ratio of integrated intensity for the first two was 4.6 ± 0.2 , indicating the presence of a naphthyl group (theory 4.6 for 7 "aromatic" and 32 "aliphatic" protons). The spectroscopic properties therefore accord with a hydrido-(naphthyl) structure (Ia), the *cis*-configuration being preferred because of the high dipole moment (6.0 D). The properties of a metal hydride are also apparent in the reaction with bromoethane which is reduced to ethane in high yield while (Ia) is converted into *trans*- $[\text{RuBr}(2\text{-C}_{10}\text{H}_7)(\text{PP})_2]$ (XIV) [eqn. (1)]. The infrared spectra of (Ia) and (XIV) are very similar, and the disappearance of the 1802 cm^{-1} band suggests that the compounds are related simply by the replacement of hydride by bromide.



In (Ia) naphthalene has undergone cleavage of the C-2-H bond (shown by tracer studies, below), and the fragments are attached to the ruthenium atom in the bivalent state.

The complexes derived from benzene, anthracene, and phenanthrene are similar, in having high dipole moments and a $\nu(\text{Ru-H})$ vibration near 1800 cm^{-1} . The phenyl and anthryl derivatives had complex multiplets at $\tau = 2.37, 3.44$ (five protons), and 2.25 (nine protons), respectively; the phenanthryl derivative was not examined.

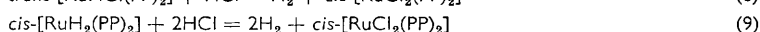
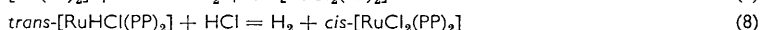
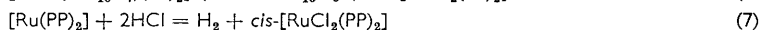
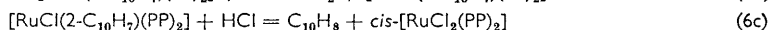
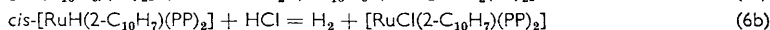
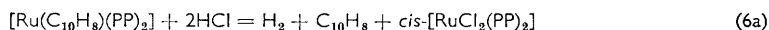
However, the form (Ia) can only be a partial description of the molecule because many chemical reactions indicate the formulation as a naphthalene complex $[\text{Ru}(\text{C}_{10}\text{H}_8)(\text{PP})_2]$ (Ib). The naphthalene is labile; a simple pyrolysis reaction takes place at $150^\circ/10^{-3}\text{ mm}$. to give naphthalene and $[\text{Ru}(\text{PP})_2]$ (II) in good yield [eqn. (2)]. Naphthalene is also liberated at room temperature on treatment with one equivalent of triethylphosphine; although no complex product could be isolated from this reaction it may well be a displacement of one neutral ligand by another, to form $[\text{Ru}(\text{PET}_3)(\text{PP})_2]$ which other experiments have shown is probably a liquid (p. 851). Iodine oxidation apparently involves reaction at the metal atom only, since hydrogen iodide was not formed [eqn. (3)]. Reaction mixtures were quenched with water at various stages in unsuccessful attempts to detect the acid. This does not rigorously exclude a two-stage oxidation mechanism [eqn. (4)], although by analogy with the hydrogen chloride reactions described below it is improbable.



The pyrolysis product $[\text{Ru}(\text{PP})_2]$ (II) might be formulated as the expected d^8 -square-planar complex of ruthenium(0) but it surprisingly contains a Ru-H stretching vibration at 1791 cm^{-1} , with an unresolved shoulder at 1815 cm^{-1} . The complex is colourless, diamagnetic, monomeric in boiling benzene, and has a dipole moment of 1.50 D. Unfortunately, solutions sufficiently concentrated to examine the n.m.r. spectrum for Ru-hydrogen resonance could not be obtained. This compound also had a dual character, behaving chemically as a zerovalent complex $[\text{Ru}^0(\text{PP})_2]$ (IIb) [eqn. (12)] but having the physical properties of a hydride $[\text{RuH}(\text{CH}_2\cdot\text{PMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PMe}_2)(\text{PP})]$ (IIa).

The reactions of these complexes and of some related authentic ruthenium hydrides with hydrogen chloride and deuterium chloride have been studied quantitatively under a vacuum, the products being analysed by mass spectrography (Table 3). The stoichiometry of each reaction was established for hydrogen chloride, and by use of these data an exact equivalent or small excess of deuterium chloride was measured out to react with a second sample of the complex. This eliminated the possibility that any significant amount of the products could exchange with excess deuterium chloride. The absence of exchange was also shown in the following model systems. An arbitrary sample of HD containing some H_2 and a smaller amount of D_2 remained unchanged with respect to exchange between isotopes when in contact with a tetrahydrofuran solution containing *cis*- $[\text{RuCl}_2(\text{PP})_2]$, naphthalene, and deuterium chloride, under conditions similar to those of the reactions. Also, the reaction between $[\text{Ru}(\text{PP})_2]$ and deuterium chloride was repeated in the presence of an added equivalent of naphthalene; the isotopic constitution of the products was unaltered and the yields were undiminished. Therefore, naphthalene is not reduced under these conditions, and it does not exchange with deuterium. All reactions with hydrogen chloride afforded hydrogen as a product, and on isotopic substitution of the reactant it appears that the hydrogen and deuterium atoms which form the gaseous product must have sufficiently long lives in solution to react with each other in random fashion. In all reactions with deuterium chloride, except that of *trans*- $[\text{RuHBr}(\text{PP})_2]$, the gaseous-product distribution was in agreement with the statistical prediction, *i.e.*, $\text{D}_2 = (1-x)^2$, $\text{HD} = 2x(1-x)$, and $\text{H}_2 = x^2$, where x = atom fraction of hydrogen and $(1-x)$ = atom fraction of deuterium. *trans*- $[\text{RuHBr}(\text{PP})_2]$ reacted very slowly compared with the other complexes which all decomposed within a few seconds, and the abnormally high yield of HD in this case may be related to the reaction rate.

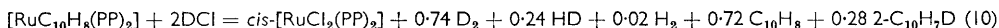
Equations (6a), (7), (8), and (9) show the observed stoichiometry of the hydrogen chloride reactions. *trans*- $[\text{RuHCl}(\text{PP})_2]$ and *cis*- $[\text{RuH}_2(\text{PP})_2]$ (III) are included as examples of authentic ruthenium hydrides and these give the expected volumes of hydrogen [eqns. (8) and (9)]. $[\text{Ru}(\text{PP})_2]$ evolves one equivalent of hydrogen, which accords with the assignment of zero oxidation state for ruthenium in this molecule, but the analogous reaction [eqn. (6a)] of the naphthalene complex in its zerovalent formulation (Ib) cannot be distinguished from the possible consecutive reactions [eqns. (6b) and (6c)] of the hydrido-(naphthyl) formulation (Ia). Equation (6a) is correct for the overall reaction, independently of mechanism, and no evidence could be found for products of naphthalene reduction. The yield of naphthalene (91.5%) was close to the calculated amount, and that of hydrogen, the possible reducing agent, exactly quantitative. $[\text{RuC}_6\text{H}_6(\text{PP})_2]$ (IV) and $[\text{RuC}_{14}\text{H}_{10}(\text{PP})_2]$ (V) underwent similar reaction with hydrogen chloride (2 equivalents), and likewise yielded hydrogen (1 equivalent).



The hydrogen chloride reactions confirm that both (I) and (II) must be either zerovalent

complexes or monohydrido-complexes of ruthenium(II), and their reactions with deuterium chloride should distinguish between these. Ideally, hydrido-complexes will give the characteristic 25 : 50 : 25 product distribution ($x = 0.50$), and a very good approximation was obtained from *cis*-[RuH₂(PP)₂] (III) where the observed value of x was 0.48. The same result would be obtained from *cis*-[RuH(2-C₁₀H₇)(PP)₂] (Ia), but [Ru(C₁₀H₈)(PP)₂] (Ib) should be oxidised to ruthenium(II) by deuterium chloride which will itself be reduced to D₂; x will then be finite only to the extent that deuterium chloride is able to exchange with its surroundings. This exchange proved to be small in these reactions.

The reaction of (I) with deuterium chloride is remarkable in that the products correspond to a mixture of those to be expected from both (Ia) and (Ib) and can only be explained by the postulated novel type of tautomerism. Equation (10) represents the data, and as no attempt was made to control reaction temperatures, these were surprisingly reproducible. They give an x value of 0.14. 2-Deuterionaphthalene was readily detected in the naphthalene product by its characteristic infrared spectrum, proving that (Ia) is the



2-naphthyl isomer. In a single instance a mass spectrogram was also obtained for the naphthalene, which was shown to contain a mole fraction of 0.38 ± 0.02 of C₁₀H₇D. This was rather higher than the fraction ($2x = 0.28$) calculated from the hydrogen-isotope analyses. The 2-deuterionaphthalene analogue [Ru 2-C₁₀H₇D(PP)₂] (VII) was also used to demonstrate that the hydrogen in the HD and H₂ in eqn. (10) originated at C-2 of the naphthalene. Only 25% of the deuterium atoms should be in the correct orientation to react with hydrogen chloride, and the product contained 3.9 volume % of deuterium, in good agreement with 25% of the x value observed in eqn. (10). This agreement excludes the possibility of appreciable exchange of solvent impurities, etc., with the deuterio-compounds during the reactions. Isotopic exchange of the ruthenium hydride prior to reaction may be eliminated since the products would then be dependent upon the deuterium chloride concentration, which is contrary to experience.

Since [Ru(PP)₂] (II) has the infrared spectrum of a ruthenium hydride, reaction with deuterium chloride should again lead to a mixture of products. The results compare closely with those obtained from (I) but the proportion of light isotope was slightly higher ($x = 0.17$). Thus tautomerism also occurs in (II).

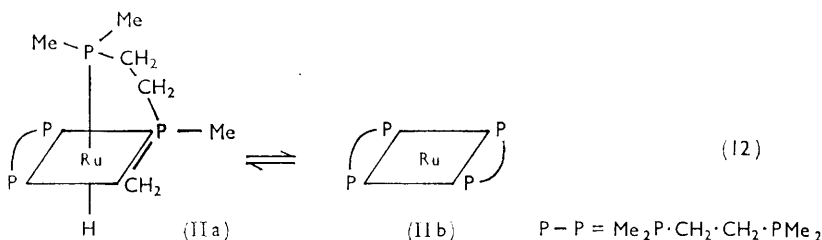
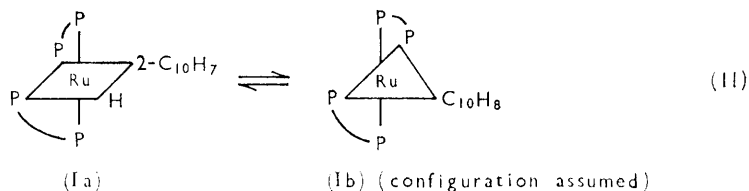
Perdeuterionaphthalene and perdeuterio-1,2-bisdimethylphosphinoethane were used to establish the origin of the hydrogen atom which gives rise to the 1800 cm.⁻¹ band in the spectrum of (II). This also allowed other assignments by comparison of the spectra of the deuterio- and hydrogen compounds, notably, the aromatic C-H bending modes were separated from the aliphatic C-H bending modes and the P-C stretching modes.

Absorption due to $\nu(\text{Ru-D})$ is to be expected near 1300 cm.⁻¹, and was first observed in *cis*-[RuHD(PP)₂] at 1303 cm.⁻¹ as a shoulder on the high-frequency side of the sharp doublet (1276, 1295 cm.⁻¹) which is probably the symmetrical deformation frequency of the methyl groups attached to phosphorus in these molecules.^{12a} This doublet is strong enough to obscure the Ru-D absorption in the 2-deuterionaphthalene complex (VII) but not in *cis*-[RuD(2-C₁₀D₇)(PP)₂] (VIII) where the isotopic shift is complete [$\nu(\text{Ru-D}) = 1294 \text{ cm.}^{-1}$] and only a small residual peak remains at 1803 cm.⁻¹. This substitution confirms that an "aromatic" hydrogen becomes bound to the ruthenium atom. The Ru-D frequency was measured accurately by synthesis of the perdeuterio-compound, *cis*-[RuD(2-C₁₀D₇){(CD_3)₂P·CD₂·CD₂·P(CD_3)₂}] (IX) [$\nu(\text{Ru-D}) = 1296 \text{ cm.}^{-1}$] whose spectrum is otherwise clear in the 1300 cm.⁻¹ region.

In the compound [Ru(PP)₂] (II) which has a Ru-H band at 1791 cm.⁻¹, the Ru-hydrogen atom comes from the diphosphine. This was shown by the pyrolysis of *cis*-[RuD(2-C₁₀D₇)(Me₂P·CH₂·CH₂·PMe₂)₂] (VIII) which gave pure perdeuterionaphthalene

¹² Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, (a) p. 321; (b) p. 76.

and the residue (II) in which the full intensity of the Ru-H absorption at 1791 cm^{-1} was restored, and by the synthesis from *cis*-[RuH(2-C₁₀H₇){[(CD₃)₂P·CD₂·CD₂·P(CD₃)₂]₂] (XI) of [Ru{(CD₃)₂P·CD₂·CD₂·P(CD₃)₂}]₂ (X) which had $\nu(\text{Ru-D})$ at 1291 cm^{-1} . The hydrogen was shown to come from a methyl group, since, in [Ru(Me₂P·CD₂·CD₂·PMe₂)₂] (XII), obtained by pyrolysis of *cis*-[RuH(2-C₁₀H₇)(Me₂P·CD₂·CD₂·PMe₂)₂] (XIII), the light isotope is bound to the metal [$\nu(\text{Ru-H}) = 1794\text{ cm}^{-1}$].



The chemical and physical evidence provides a reasonable description of the "arene" complexes and of [Ru(PP)₂] in terms of a novel tautomerism [eqns. (11) and (12)]. In the solid state the naphthalene complex must be *cis*-[RuH(2-C₁₀H₇)(PP)₂] (Ia), but on solution it must tautomerise to give a small concentration of the much more reactive (Ib), and similarly for (IIa) and (IIb). Although several hydrido(alkyl) analogues of (Ia), and also *trans*-[RuH(C₆H₅)(PP)₂], have been described,¹³ no evidence for this type of tautomerism has previously been noted.

In the complex (Ib) the naphthalene can use only two electrons in bonding to the metal, because the ruthenium atom can accommodate only 10 additional electrons in low-energy orbitals (8 from the phosphine ligands and 2 from naphthalene). The naphthalene complex (Ib) may thus be represented either as a 5-co-ordinated complex of ruthenium(0) in which the naphthalene co-ordinates as a neutral ligand, after the manner of a mono-olefin, as benzene does in C₆H₆CuAlCl₄,¹⁴ or it may be represented as a 6-co-ordinated complex of ruthenium(II) in which the naphthalene behaves as a co-ordinated di-anion. In this case the metal would be σ -bonded to two carbon atoms in the hydrocarbon, cf. [Rh(C₅H₅){C₆(CF₃)₆}] and similar substances¹⁵ where both π - and σ -complexing occurs.

We favour the ruthenium(0) structure, as assumed in eqn. (11), because no reduction of the hydrocarbon ligand was observed in its displacement by hydrogen chloride, and this would be expected if the hydrocarbon were behaving as a co-ordinated di-anion. Also, it is not possible to write a structure in which the phosphine behaves as a di-anion in the analogous 4-co-ordinate [Ru⁰(PP)₂] (IIb). The complex (Ib) need not have a trigonal-bipyramidal configuration as shown in eqn. (11); it might equally well have a square-pyramidal structure. The hydride migration in the interconversion (Ia) \rightleftharpoons (Ib) may be intermolecular, but it is much more likely to be intramolecular, and the aromatic nucleus clearly does not become detached from the ruthenium atom during the migration, because the pyrolysis could not be reversed by heating [Ru(PP)₂] (II) with a large excess of

¹³ Chatt and Hayter, *J.*, 1963, 6017.

¹⁴ Turner and Amma, *J. Amer. Chem. Soc.*, 1963, **85**, 4046.

¹⁵ Churchill and Mason, *Proc. Chem. Soc.*, 1963, 365.

naphthalene at 110° for 24 hours; also, there was no hydrogen exchange between the phosphine ligand and the naphthalene.

The high dipole moments of the series of hydrocarbon complexes in their *cis*-hydrido(aryl) configurations, as (Ia), reveal appreciable effects due to π -bonding between octahedral ruthenium(II) and the antibonding orbitals of the aromatic radicals. The Ru-C bond-order (back donation) should be enhanced by delocalisation of the π -electrons as the number of fused rings increases, and accordingly the dipole moments (in parentheses below) show that the hydrogen nuclei are more negative in the expected sequence, *viz.*, phenyl (5.30) < naphthyl (6.00) < phenanthryl (6.25) \approx anthryl (6.35).

The main features of the infrared spectra are common to all four aryl complexes but differences arise in the highly characteristic C-H out-of-plane deformation frequencies and the C-C ring stretching frequencies. The assignments in Table I are based on the variations in the spectra. They have been confirmed for the naphthyl compound (Ia) by their presence in the spectra of the deuteriophosphine derivatives (XI) and (XIII) and absence from the deuterionaphthyl derivatives (VIII) and (IX). The bands at 737 and 814 cm^{-1} are typical of the two strong bands that recur in compounds having the 2-naphthyl group (*e.g.*, 2-methylnaphthalene,¹⁶ 741, 812 cm^{-1}). Similarly, those at 692 and 730 cm^{-1} of (IV) fall within the accepted limits^{12b} for the phenyl group.

The stretching frequencies of metal-hydrogen bonds in related series of octahedral and square-planar complexes are dependent on both the metal and the ligand in “*trans*” position.¹⁷ The 1800 cm^{-1} band occurs for *cis*-[RuH₂(PP)₂] (III) and is probably characteristic of the system *trans*-R₃P-Ru-H in octahedral complexes. Complexes with hydrogen *trans* to tertiary phosphines are not common, presumably because of the inherent instability of a *trans*-arrangement of ligands both of high *trans*-effect. However, in our chelate ruthenium(II) complexes the possible configurations are limited, and the 1800 cm^{-1} band occurs with remarkable constancy, both in the hydrido(aryl) complexes and in [Ru(PP)₂] (II). This is the best evidence that the hydrogen has indeed been transferred completely to the ruthenium atom and does not remain weakly bound to carbon.

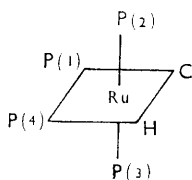
Only *cis*-[RuH(2-C₁₀H₇)(PP)₂] was studied in the n.m.r. spectrum to low-field of tetramethylsilane. The resonances occur in the same region as those of *cis*-[RuH₂(PP)₂], and the spectrum has two doublets at $\tau = 17.6$ and 19.8. The electronic interaction with the *trans*-phosphorus will be strong, and a large *J* value would be expected for the ensuing doublet. If P(4) proves to be in a similar environment to the equivalent pair P(2) and P(3) then the three *cis*-ligand atoms will split the doublet into two quartets. Assuming the 1 : 3 : 3 : 1 intensity pattern, the outer components might be within the noise level, giving a spurious double doublet. The double quartet is the simplest multiplet that could arise from (Ia) and the data are therefore to be regarded as inadequate.

The physical properties and reactions of [Ru(PP)₂] (II) suggest that it also tautomerises [eqn. (12)], and like the naphthalene compounds the solid and the main component in solution is the hydride (IIa). Highly reactive reagents such as hydrogen chloride and iodine react with the ruthenium(0) complex (IIb), but naphthalene, which might have given (Ib) and hence (Ia), does not react, presumably because the concentration of (IIb) in the equilibrium is too low.

There is only one hydrogen atom attached to the metal in (IIa) because the 1800 cm^{-1} band in it and (Ia) have relative intensities similar to those of bands common to both spectra. However, in (IIa) there is a shoulder of medium intensity which becomes resolved after repeated recrystallisation. In (IIa) the metal must be essentially octahedrally co-ordinated, but the small P-CH₂ unit, having lost a hydrogen atom, must occupy two co-ordinating positions, and there must be considerable distortion from the

¹⁶ Dahn, Zoller, and Solms, *Helv. Chim. Acta*, 1954, **37**, 565.

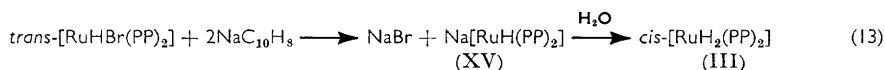
¹⁷ Chatt, *Proc. Chem. Soc.*, 1962, 318.



regular octahedron. The $\nu(\text{Ru-H})$ of 1791 cm^{-1} suggests that it contains the *trans*-P-Ru-H atomic grouping and so has the *cis*-configuration as shown in (IIa) [eqn. (12)]. On the other hand, the low dipole moment (1.5 D) implies either a *trans*-configuration, which is unlikely in view of the close analogy to the naphthalene compounds, or, more likely, such distortion that the phosphorus atom attached to the $\text{CH}_2\text{-Ru}$ group is held so close to the CH_2 group that its P-Ru bond dipole moment is in partial opposition to that of the phosphorus atom *trans* to CH_2 . This distortion would thus lead to a more symmetrical distribution of the highly charged phosphorus atoms. A further minor factor, affecting the charge distribution as compared with the naphthyl compounds, may arise because alkyl groups in complex compounds of metals having filled *d*-orbitals carry less negative charge than aryl groups,¹⁸ leading in this case to a slightly more symmetrical charge distribution.

We can attribute the reactions which involve the cleavage of the C-H bond in naphthalene or in the tertiary diphosphine ligand to the likely properties of square-planar ruthenium(0), the requisite combination being the very strong reducing power of the metal together with a vacant site in the co-ordination shell which allows attachment of the reacting species. That the latter is the key property is emphasised by the course of some of the preparations. The ruthenium(0) complex retains affinity for feebly basic ligands, and under certain conditions can probably be further reduced. Tetrahedral ruthenium(−II) has the electronic configuration of the next inert gas and should be thermodynamically stable.

Triethylphosphine replaces naphthalene from (Ib) and would therefore be expected to inhibit the formation of aryl complexes during the reduction reactions. In the presence of triethylphosphine *trans*- $[\text{RuCl}_2(\text{PP})_2]$ reacts with sodium-naphthalene giving a very soluble product that crystallises from *n*-pentane at -78° . This is probably the 5-co-ordinate compound $[\text{Ru}(\text{PET}_3)(\text{PP})_2]$, but unfortunately it softened below room temperature and could not be purified. Similarly, an anionic ligand which cannot itself be cleaved from the metal by reduction causes the reduction to follow another course. The reduction of *trans*- $[\text{RuHBr}(\text{PP})_2]$ gives neither a *d*⁷-complex nor a dimer with a metal-metal bond but is reduced directly to the ruthenate(0) salt (XV). This can be hydrolysed to *cis*- $[\text{RuH}_2(\text{PP})_2]$ [eqn. (13)], and it also reacts with deuterium oxide to yield



cis- $[\text{RuHD}(\text{PP})_2]$. In a similar reaction, the dichloride was reduced in tetrahydrofuran by molten potassium. The crude product showed no ruthenium hydride vibration in the infrared region but on hydrolysis gave only a small yield (*ca.* 5%) of *cis*- $[\text{RuH}_2(\text{PP})_2]$. It seems likely that $[\text{Ru}(\text{PP})_2]$ will have only transient existence and that it accepts two further electrons to form $\text{K}_2[\text{Ru}(\text{PP})_2]$. Small yields of (III) could also be isolated from the reaction mixtures when (I) was prepared from *cis*- $[\text{RuCl}_2(\text{PP})_2]$ and they presumably have a similar origin.

cis- $[\text{RuH}_2(\text{PP})_2]$ is of special interest since it provides the authentic example of a hydrido-ruthenium complex in which the hydride is *trans* to the phosphorus of bisdimethylphosphinoethane. This is not a common stereochemical arrangement especially since lithium aluminium hydride reduction of *cis*- $[\text{RuCl}_2(\text{ditertiary phosphine})_2]$ gave the corresponding *trans*-isomers of $[\text{RuH}_2(\text{ditertiary phosphine})_2]$ ¹⁹ [ditertiary phosphine = $\text{Et}_2\text{P}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{PET}_2$ or *o*- $\text{C}_6\text{H}_4(\text{PET}_2)_2$]. However, reduction of *cis*- $[\text{RuCl}_2(\text{PP})_2]$ under the same conditions affords variable yields of (III) only, and the crude product shows no infrared absorption near 1615 cm^{-1} as found in the *trans*-isomers. *cis*- $[\text{RuH}_2(\text{PP})_2]$ is a low-melting colourless solid (m. p. 82°) which sublimes in a vacuum and is extremely

¹⁸ Chatt and Shaw, *J.*, 1959, 4020.

¹⁹ Chatt and Hayter, *J.*, 1961, 2605.

soluble in hydrocarbon and ether solvents. Both the solid and its solutions oxidise rapidly in the air.

The stereochemistry of *cis*-[RuH₂(PP)₂] has been established from its dipole moment. The value of 3.15 D contrasts with the zero moments of *trans*-octahedral species, and the derived P-Ru-H group moment of 2.2 D compares well with the moment (2.5 D) of the group P-Ir-H in *trans*-[IrHCl₂(PEt₃)₃]. These moments may appear low for compounds in which hydrogen behaves as an anionic ligand, but they are consistent with the moments of other hydrido-complexes.¹⁷

The infrared spectrum of *cis*-[RuH₂(PP)₂] has a very strong band at 1806 cm.⁻¹, which is broad and may be the expected doublet Ru-H stretching modes which have not been resolved. The range 1791—1806 cm.⁻¹ for ν (Ru-H) with hydrogen *trans* to phosphorus should be compared with the very low values observed for *trans*-dihydrido-complexes *e.g.*, *trans*-[RuH₂(Et₂P·CH₂·CH₂·PEt₂)₂] has ν (Ru-H) = 1615 cm.⁻¹.¹⁹ The difference may be related to the very high *trans*-labilising effect of the hydrido-group even when compared with the tertiary phosphine,¹⁷ and should be a diagnostic feature of the stereochemistry.

The n.m.r. spectrum of *cis*-[RuH₂(PP)₂] shows an unsymmetrically disposed complex multiplet of at least seven lines near τ = 18.6. Although the multiplet structure could not be analysed, the chemical shift is similar to that in *cis*-[RuH(2-C₁₀H₇)(PP)₂].

EXPERIMENTAL

All preparations were carried out in an atmosphere of dry nitrogen, using a glove-box. Following the usual methods of purification, benzene and tetrahydrofuran were refluxed with sodium-benzophenone complex prior to the final distillation. Petroleum for crystallisations was refluxed in a stream of nitrogen to remove oxygen. M. p.s are corrected and were determined in evacuated sealed tubes.

cis-Hydrido-(2-naphthyl)di-(1,2-bisdimethylphosphinoethane)ruthenium(II) (I).—Sodium-naphthalene was prepared by shaking a tetrahydrofuran solution (100 ml.) of naphthalene (1.6 g., 2.4 mol.) with an excess of sodium for 3 hr. The reducing agent was added dropwise to a stirred solution of *trans*-dichlorodi-(1,2-bisdimethylphosphinoethane)ruthenium(II)²⁰ (2.5 g., 1.0 mol.) in tetrahydrofuran (25 ml.) during 10 min. until the green colour became permanent. Solvent was distilled from the mixture at 25°/9 mm.; naphthalene also sublimed at 9 mm. but only after slight warming. The product was separated from sodium chloride with several small portions of boiling petroleum (b. p. 80—100°) and commenced to crystallise immediately after filtration as very pale yellow prisms (1.9 g., 68%) [Found: C, 50.2; H, 7.7%; *M* (ebullioscopy, 1.045% solution in benzene), 519. C₂₂H₄₀P₄Ru requires C, 49.9; H, 7.6%; *M*, 529]. Further crystallisation gave almost colourless material. The reduction is accompanied by formation of a wine-red colour which fades to pale brown on prolonged standing. The red colour is also dispelled by addition of a few drops of 5% water-tetrahydrofuran, and is probably due to the presence of ruthenium(—II). The preparation follows the same course when the starting material is the corresponding *cis*-dichloride, but following removal of naphthalene up to 5% yield of *cis*-dihydridodi-(1,2-bisdimethylphosphinoethane)ruthenium(II) (III) may be obtained by distillation at 100°/10⁻³ mm.

trans-[RuCl₂(Me₂P·CH₂·CH₂·PMe₂)₂] was also used to prepare *cis*-hydrido(anthryl)di-(1,2-bisdimethylphosphinoethane)ruthenium(II) (V), orange prisms [from petroleum (b. p. 80—100°)], 74% yield following reduction with disodium-anthracene [Found: C, 53.8; H, 7.4%; *M*, (ebullioscopy, 1.417% solution in benzene), 569. C₂₆H₄₂P₄Ru requires C, 53.8; H, 7.45%; *M*, 579], and *cis*-hydrido(phenanthryl)di-(1,2-bisdimethylphosphinoethane)ruthenium(II) (VI), colourless prisms [from petroleum (b. p. 80—100°)], 50% yield following reduction with sodium-phenanthrene (approx. Na_{1.5}C₁₄H₁₀) (Found: C, 53.0; H, 7.22%).

cis-Hydrido(phenyl)di-(1,2-bisdimethylphosphinoethane)ruthenium(II) (IV).—*trans*-Dichlorodi-(1,2-bisdimethylphosphinoethane)ruthenium(II) (0.74 g., 1.0 mol.) was dissolved in 5% benzene-tetrahydrofuran (10 ml.) and sealed into an ampoule with potassium (0.137 g.,

²⁰ Chatt and Hayter, *J.*, 1961, 896.

2.0 atoms). The vessel was shaken vigorously in a stream of warm air at about 80° and potassium chloride separated as the molten metal dissolved during 4 hr. The resultant solution was filtered to remove much of the potassium chloride and traces of potassium metal and distilled at 9 mm. to remove solvents. The residue was a low-melting solid most of which dissolved readily in petroleum (b. p. 40–60°) to give a solution from which the complex crystallised as colourless needles at –15° (0.43 g., 54%) [Found: C, 45.2; H, 8.1%; *M* (ebullioscopy, 0.679% solution in benzene), 534. $C_{18}H_{38}P_4Ru$ requires C, 45.0; H, 8.2%; *M*, 479].

Hydrido-(2,5-dimethyl-2,5-diphosphahex-1-yl)(2,5-dimethyl-2,5-diphosphahexane)ruthenium(II)—(II).—The naphthyl complex (I) (0.97 g.) was heated in a small furnace at 150–155°/10^{–3} mm. for 24 hr. with continuous pumping. The volatile naphthalene was collected in a U-tube maintained at –78° and was purified by fractional sublimation and condensation (m. p. 80°; picrate had m. p. 149–151°). The non-volatile residue of effloresced crystals was the substantially pure *pyrolysis product* which had undergone only slight decomposition and was still almost colourless when finely divided. It crystallised from petroleum (b. p. 80–100°) as large colourless rhombs (0.47 g., 64%) but with substantial losses [Found: C, 35.6; H, 8.0%; *M* (ebullioscopy, 0.266% solution in benzene), 397. $C_{12}H_{32}P_4Ru$ requires C, 35.9; H, 8.05%; *M*, 401].

cis-Dihydridodi-(1,2-bisdimethylphosphinoethane)ruthenium(II) (III).—Sodium-naphthalene (from 0.179 g. naphthalene, 2.4 mol.) in tetrahydrofuran (10 ml.) was added dropwise to *trans*-hydridobromodi-(1,2-bisdimethylphosphinoethane)ruthenium(II)¹⁹ (0.28 g., 1.0 mol.) in tetrahydrofuran (4 ml.), with stirring. An intense red colour developed at once and this deepened to make the end-point unsharp. When a permanent green colour appeared 5% water-tetrahydrofuran was added cautiously until the solution just became colourless. This stage of the reaction was not accompanied by effervescence and care was taken not to add any excess of water. The solvent and some naphthalene were removed at 9 mm. and the soluble portion of the reaction mixture extracted with petroleum (b. p. 40–60°) which yielded an oily crude *product* which was purified by vacuum-distillation along a 10-mm. glass tube heated by a small furnace maintained at 80–90°. *cis*-[$RuH_2(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2$] commenced to distil just below the melting point and collected as a viscous colourless liquid in the cooler part of the tube. It solidified on standing (0.080 g., 34%) [Found: C, 36.0; H, 8.5%; *M* (cryoscopy, 1.21% solution in benzene), 409. $C_{12}H_{34}P_4Ru$ requires C, 35.8; H, 8.25%; *M*, 403]. The complex was also prepared from *trans*-dichlorodi-(1,2-bisdimethylphosphinoethane)ruthenium(II)²⁰ (0.4 g.) in tetrahydrofuran (5 ml.) by reduction with molten potassium (0.07 g.). The method was that used to prepare (IV) (above) except that benzene was not added to the medium. The orange solution was filtered and solvent removed from a small aliquot in a vacuum. The residue was shown from its infrared spectrum to be free from hydrido-ruthenium complexes. Moist tetrahydrofuran was added to the bulk of the solution until the colour had been dispelled, after which (III) was isolated as in the previous experiment (0.03 g., 9%). Lithium aluminium hydride (0.10 g. in excess) reduction of *cis*-dibromodi-(1,2-bisdimethylphosphinoethane)ruthenium(II)²⁰ (1.0 g.) in tetrahydrofuran (50 ml.) (cf. ref. 19) gave a colourless solution, and from the crude product, obtained following distillation of the solvent, (III) was extracted with light petroleum. The yield after purification was 0.06 g. (8.5%).

Reactions with iodine. The interaction of *cis*-[$RuH(2-C_{10}H_7)(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2$] and iodine was studied by titrations in both tetrahydrofuran and benzene solutions. Iodine oxidation led to the formation of a golden yellow colour, and after the addition of 1.0 equiv. of halogen a deep red end-point was reached. A positive iodine test with an external starch-iodide indicator was not obtained until a further 0.5 equiv. had been added. Thus, 0.0322 g. of complex on titration with 0.0392N-iodine in tetrahydrofuran required 3.09 ml. (0.991 equiv.) to the first end-point (Ru^{II}) and a further 1.59 ml. (1.50 equiv.) to the second (Ru^{III}). The solvent was removed at 0°/9 mm., and then, on warming, naphthalene sublimed and was collected by fractional condensation. After crystallisation from petroleum (b. p. 40–60°) it was identified from its infrared spectrum and m. p. of 80°. The residue crystallised from acetone as red elongated prisms which decomposed to *trans*-di-iododi-(1,2-bisdimethylphosphinoethane)ruthenium(II), m. p. 302° with prior sublimation above 250° (lit.,²⁰ 302–304°), on standing. The infrared spectrum of the suspected $Ru(III)$ complex was very similar to that of *trans*-[$RuI_2(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2$] but had an additional strong band at 720 cm.^{–1}. When carried out in benzene, the first stage of the oxidation of (I) (0.0641 g.)

required 7.00 ml. of 0.0352*N*-iodine in benzene and was accompanied by crystallisation of *cis*-[RuI₂(Me₂P·CH₂·CH₂·PMe₂)₂]. The solvent was carefully distilled and the residue of *cis*-diiodide was washed with boiling petroleum (b. p. 40–60°) and dried (0.076 g., 96.5%). When recrystallised from ethanol it had m. p. 291° (lit.,²⁰ 291°), and was identical with an authentic specimen (infrared spectrum). Reactions in benzene were quenched with water at various stages and in all cases the aqueous extract had a neutral reaction.

Similarly, di-(1,2-bisdimethylphosphinoethane)ruthenium (0.0260 g.) in tetrahydrofuran (10 ml.) required 3.23 ml. of 0.0414*N*-iodine solution to develop a permanent red colour. Removal of the solvent gave crude *cis*-[RuI₂(Me₂P·CH₂·CH₂·PMe₂)₂] (0.0475 g., 112%), m. p. 291° (from ethanol), identified by comparison with the authentic material.

Reactions with hydrogen chloride and deuterium chloride. Gases and anhydrous solvents were handled *in vacuo* on a semimicro scale using a greaseless Stock-type apparatus. A weighed, compressed pellet of the complex was dropped through a constriction into a reaction bulb (50-ml.) which was evacuated and sealed. Tetrahydrofuran (2 ml. liquid, distilled directly from sodium-benzophenone complex) and a measured excess of hydrogen chloride were then condensed on to the sample through a break-seal side-arm, and the vessel was again isolated at a second constriction. On warming, effervescence commenced near 0° and the reaction was complete within a few seconds. A second break-seal side-arm was used to admit the hydrogen to the Töpler system where it was pumped into a manometer of known volume. Excess of hydrogen chloride and the solvent were distilled away at –22° into a bulb containing water, and the acid was determined by titration against *N*/20 potassium hydroxide. The residue in every case was *cis*-[RuCl₂(Me₂P·CH₂·CH₂·PMe₂)₂], which crystallised from benzene, and in appropriate cases the aromatic hydrocarbon was also isolated. After the stoichiometry had been established, a second sample of complex was treated with a measured small excess of deuterium chloride. The volume of the D₂–HD–H₂ mixture evolved was checked in the Töpler system which was then used to re-cycle the gas into a storage bulb for subsequent mass spectrographic analysis. In these experiments, after removal of solvent, the deuterated naphthalene was recovered by fractional condensation at –16°.

Reactions with bromoethane. Bromoethane, purified in the vacuum line by distillation at –45° and fractional condensation at –95°, had a saturated vapour pressure of 167 mm./0°. A pellet of *cis*-[RuH(2-C₁₀H₇)(PMe₂·CH₂·CH₂·PMe₂)₂] (I) (0.0677 g.) was sealed into a bulb under a vacuum, and the bromoethane (3 ml. liquid) was then condensed on to it. After a reaction time of 4 hr. at 20°, the volatile compounds were distilled at –22°, and separated by fractional condensation at –126°. In this way, ethane (2.49 ml. at s.t.p., 86.7%) was isolated from the excess bromoethane. It was identified from its infrared spectrum which also indicated a trace of ethylene. The reaction residue was *trans*-bromo-(2-naphthyl)di-(1,2-bisdimethylphosphinoethane)ruthenium(II) (XIV) which crystallised from benzene as very pale yellow tablets having a molecule of solvent of crystallisation which was marked by infrared absorption at 671 cm.^{–1} that had not been present in the crude material (Found: C, 48.5; H, 6.5. C₂₈H₄₅BrP₄Ru requires C, 48.9; H, 6.6%). A similar reaction was carried out with (II) but no well-defined product could be isolated.

Synthesis of Compounds Labelled with Deuterium.—Deuterium chloride. Deuterium oxide (99.97%) (*ca.* 50 mg.) was introduced, through a constriction, into a reaction bulb (50-ml.) which was cooled, evacuated, and sealed off. Boron trichloride (*ca.* 50–75 ml. at s.t.p.) was then introduced through a break-seal side-arm. After reaction in the closed system at 20° the vessel was opened to a vacuum line and deuterium chloride was purified by successive distillations at –126°. The excess of boron trichloride was used to prevent the formation of DCl–D₂O azeotrope. All sections of the vacuum line were subjected to prolonged “flaming” prior to each transfer of deuterium chloride.

Deuterium hydride. Deuterium oxide (99.97%) was condensed at –196° into a reaction bulb containing lithium aluminium hydride. On warming, reaction took place at about 0° after which the deuterium hydride was removed and pumped through a spiral at –196° into storage bulbs [Found (mass spectrography analysis), D₂, 0.8; HD, 96.0; H₂, 3.2%].

Labelled complexes were prepared by duplication of the methods detailed above. Starting materials were carefully purified and checked by microanalysis. The complexes were prepared on a small scale and only infrared spectra and melting points were recorded. The melting points differed little from those of the corresponding light-hydrogen compounds and mixed melting points were not depressed but had wider ranges. (CD₃)₂P·CD₂·CD₂·P(CD₃)₂ and

$\text{Me}_2\text{P}\cdot\text{CD}_2\cdot\text{CD}_2\cdot\text{PMe}_2$ were prepared by the stepwise alkylation method²⁰ by use of commercial CD_3Br and $\text{ClCD}_2\cdot\text{CD}_2\text{Cl}$ where appropriate. However, to attain exact stoichiometry in a small-scale preparation, the sodamide was added as weighed samples of freshly prepared solid and not as a slurry in liquid ammonia. By use of these ditertiary phosphines, the compounds *trans*- $[\text{RuCl}_2\{(\text{CD}_3)_2\text{P}\cdot\text{CD}_2\cdot\text{CD}_2\cdot\text{P}(\text{CD}_3)_2\}_2]$, m. p. 291.5—294° (Found: C, 28.6. $\text{C}_{12}\text{D}_{32}\text{Cl}_2\text{P}_4\text{Ru}$ requires C, 28.6%), and *trans*- $[\text{RuCl}_2(\text{Me}_2\text{P}\cdot\text{CD}_2\cdot\text{CD}_2\cdot\text{PMe}_2)_2]$, m. p. 291—296° (Found: C, 30.0. $\text{C}_{12}\text{H}_{24}\text{D}_8\text{Cl}_2\text{P}_4\text{Ru}$ requires C, 30.0%), were prepared.²⁰ The hydrogen analogue had m. p. 299°. Commercial C_{10}D_8 had m. p. 80° (Found: C, 88.2. Calc. for C_{10}D_8 : C, 88.2%).

TABLE 4.
Dipole moment data (estimated values in parentheses).

Comp.*	$10^3\omega$	$\Delta\epsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	τ^P	ϵ^P	σ^P	μ (D)
(I)	5.275	7.998	—	—	—	—	—	—
	7.558	8.014	—	—	—	—	—	—
	22.46	—	13.22	—	—	—	—	—
	24.76	—	13.30	—	—	—	—	—
	7.618	—	—	0.394	—	—	—	—
	7.422	—	—	0.392	917.7	157.6	736.5	6.00
	2.761	0.984	—	—	—	—	—	—
(II)	2.530	1.040	—	(0.39)	167 †	(106)	45.5 †	1.5 †
(III)	2.362	3.117	—	—	—	—	—	—
	3.298	3.077	—	—	—	—	—	—
	28.04	—	7.894	—	—	—	—	—
	26.61	—	7.738	—	—	—	—	—
	6.613	—	—	0.363	—	—	—	—
	6.757	—	—	0.414	327	108	202	3.15
	2.919	6.956	—	—	—	—	—	—
(IV)	3.584	6.920	—	(0.39)	735 †	(140)	573 †	5.3 †
(V)	2.021	8.214	—	—	—	—	—	—
	1.721	8.169	—	(0.39)	1024 †	(175)	823 †	6.35 †
(VI)	2.363	7.932	—	—	—	—	—	—
	2.344	8.026	—	(0.39)	1001 †	(175)	800 †	6.25 †
(XIV)	2.250	1.301	—	—	—	—	—	—
	1.809	1.250	—	(0.40)	459 †	(159)	276 †	2.3 †

* See Table 1. † Using estimated values of refractivity and density.

2-Deuterionaphthalene. 2-Naphthyl-lithium was prepared in ether, and the solution was evaporated in a vacuum. The residue was pumped at 10^{-6} mm. for 4 hr. to remove traces of naphthalene, and then deuterium oxide was condensed on to the solid. On warming, reaction was complete within a few minutes and the $2\text{-C}_{10}\text{H}_7\text{D}$ was isolated by ether extraction and fractional condensation of the *product*, m. p. 80° (Found: C, 92.9. Calc. for $\text{C}_{10}\text{H}_7\text{D}$: C, 92.9%).

Five labelled analogues of the naphthyl complex (I) were prepared, and in three cases their pyrolysis reactions were also studied.

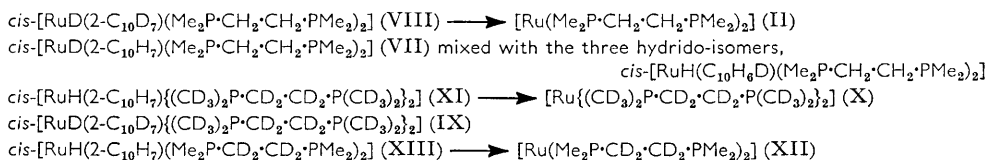


Table 4 records the dipole moment data. These were obtained as previously,¹⁸ and the symbols have the same meaning.

We thank Mr. R. A. Saunders and Mr. S. Duckworth for mass-spectrographic analyses, Dr. E. F. Mooney for some of the n.m.r. spectra, and Dr. L. E. Orgel for a helpful discussion.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, PETROCHEMICAL AND POLYMER LABORATORY,
P.O. BOX 11, THE HEATH, RUNCORN, CHESHIRE. [Received, April 17th, 1964.]